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INVESTIGATION OF OXIDE AND FLUORIDE HOSTS
FOR BLUE-GREEN LASERS

By

R.F. Belt, R. Uhrin and E. Niemczyk

Final Report
October 1, 1982 - January 31, 1985
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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Mixed crystals of the perovskite type structure of the system $La\ Al_{1-x}\ Sc_x\ O_3$ were examined over the compositions of $x=0.15-0.30$. Single crystals were grown from melts in iridium crucibles using the Czochralski method. Seed crystals of (111) pure $La\ Al\ O_3$ were used. The growth atmosphere was controlled at 99.75% N_2 and 0.25% H_2. Dopants of Ce^{3+} were maintained at 0.01-0.05 atomic per cent. Preliminary work on poly-crystalline materials showed that blue-green luminescence at 485 nm was

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found. The grown crystals had various amounts of Sc incorporated and were usually translucent. At the x=.30 formulation of melt, about 60 - 75% of Sc is believed to enter the crystal. No direct evidence was found for ordered type structures. The phase data, compositions, crystal quality, luminescence data, and x-ray results are discussed.

Several mixed fluorides were examined for possible blue-green emission by doping with rare earths. Among the host compositions was $K\ Mg\ Y_3\ F_{12}$, a crystal which could be doped with transition elements and rare earths. A sizeable effort provided fairly good single crystals for future seeds. Several polycrystalline preparations were made with Ce^{3+}, Pr^{3+}, Ti^{3+}, Nd^{3+}, Cr^{3+}, and Er^{3+}.

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ABSTRACT

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Several mixed fluorides were examined for possible blue-green emission by doping with rare earths. Among the host compositions was $KMgY_3F_{12}$, a crystal which could be doped with transition elements and rare earths. A sizeable effort produced fairly good single crystals for future seeds. Several polycrystalline preparations were made with Ce^{3+}, Pr^{3+}, Ti^{3+}, Nd^{3+}, Cr^{3+}, and Er^{3+}.

FORWARD

This final report describes research efforts on the preparation of single crystal oxide and fluoride hosts. All crystals were doped with Ce^{3+} in an attempt to obtain blue-green lasers which may operate near 485 nm. The report relates work performed in the period of October 1, 1982 to January 31, 1985. All work was done under Contract N 00014-83-C-0072. The research was coordinated under a program of Dr. Van O. Nicolai of the Office of Naval Research.

All physical preparations were completed in the laboratories of Airtron Division of Litton Industries, 200 E. Hanover Avenue Morris Plains, New Jersey 7950. The program was directed by Dr. Roger F. Belt. Mr. Robert Uhrin served as Senior Staff Engineer for oxides and Mr. Edward Niemczyk for fluorides. Ms. Karen Grimes was the Technician. Laser optical tests were performed at the Naval Research Laboratory through the courtesy of Dr. Leon Esterowitz. The fluoride preparations were run by Mr. John Yorston. The report was prepared by Dr. Roger Belt, Mr. Robert Uhrin and Mr. Edward Niemczyk. It was released for publication in August 5, 1985.

1.0 Introduction

Solid state lasers which operate in the blue-green have been a major goal of the Navy for many years. The search for these has centered on the discovery of ideal host crystals which will provide luminescence at desirable wavelengths when doped with particular rare earth ions. The latter are ions which are capable of $4f \rightarrow 5d$ transitions. They include Ce^{3+}, Eu^{2+}, Pr^{3+}, Tm^{3+}, Er^{3+}, or Nd^{3+} which have symmetry allowed broad bands. These potential lasers can be pumped with broad band sources and may even be tunable under some circumstances. The simplest ion to work with has been Ce^{3+} since it possesses only one 4f electron. The luminescence of Ce^{3+} in various host crystals has been studied for many years because of applications to CRT phosphors, lasers, and radiation detectors. It is well known that the emission of Ce^{3+} is broad band and very sensitive to the primary coordination, i.e., the exact crystal structure of the host. The early work of Blasse[1,2] showed that both ultraviolet emission around 300-400 nm and visible emission near 525-625 nm are possible. The energy level splitting for $5 d^1$ levels is actually reversed for octahedral and cubic coordination. The appropriate shifts in emission wavelengths are generated mainly through the cubic and highly symmetric laser hosts. However, one must avoid excited state absorption[3], similar to what occurs in Ce^{3+}:YAG. This suggests a high band gap host prefer-

ably above 50,000 cm^{-1} (6.2 ev). Early work at Airtron and other laboratories suggest that continued investigations with perovskite structures offer good possibilities for blue-green lasers.

An ideal laser host for blue-green operation should have the following properties:

1. The luminescence with Ce^{3+} or other rare earth should be centered around 450 - 500 nm. This suggests the near cubic site symmetry; the crystal structure need not be cubic.

2. The host band gap should be 6 ev or higher for oxide or fluoride.

3. A high radiative lifetime and high fluorescent quantum yield for Ce^{3+} or the rare earth are desirable.

4. Incorporation of a single oxidation state if Ce^{3+} is used, thus a minimum of Ce^{4+}.

5. Freedom from severe color center formation or defect oxide production during growth or optically pumping should occur.

6. A hard, refractory, chemically inert, large single crystal must be grown in high optical quality. No difficulties should occur with crucibles, phase relations, or atmospheres of growth.

7. The crystal should be grown preferably by the Czochralski method in available commercial equipment.

Nearly two years ago Airtron began preliminary work on mixed perovskites for laser hosts. The perovskite structure was chosen because of the unique coordination in the prototype ABO_3 compound. Most perovskites[4] are cubic crystal structure or through slight distortions, may possess a lower symmetry hexagonal or orthorhombic variation. In the normal ABO_3 type perovskite, the A ion possesses a coordination of 12 oxygen ions while the B ion has 6 oxygen ions. The combined charges of the A and B ions is six; thus many new combinations are possible where A is of valence 1, 2, and 3 and B is of valence 5, 4, 3 respectively. Naturally A and B can be simple ions or several sub-ions in proper amounts to maintain overall charge balance. It is appropriate to search for those perovskites which may retain the ideal cubic crystal structure. However, the coordination of the doping ion and its environment (near neighbors and second near neighbors) actually determine the precise position of fluorescent emission bands. It is of utmost importance to avoid phase transitions, twinning, or other structural behavior which may render the crystal difficult to grow or impossible to use. Thus the important host crystal La Al O_3 very early was found[5] to have a phase transformation and twins. The latter were always detrimental to high laser

rod quality[6].

Our first perovskites involved compositions of the type $La_{.5} Ba_{.5} Ta_{.25} Al_{.75} O_3$ doped with 0.01% Ce^{3+} introduced as $Ce O_2$. However, these proved to be difficult to grow in pure form by means of the Czochralski method. Furthermore, the fluorescence emission of even the polycrystalline material occurred in the orange region (580-620 nm) under ultraviolet excitation. Attempts were made in growth under N_2 and H_2 atmospheres. Even these failed to give any blue-green emission. This work was performed in the period of May - July, 1981. In September of that same year, the first experiments were performed on sintered powders in the $La Al_{1-x} Sc_x O_3$ system doped with Ce^{3+}. These experiments were suggested by Dr. Van O. Nicolai of the Office of Naval Research. Our preparation of powders were done under a N_2 - H_2 atmosphere and gave blue-green emission under ultraviolet excitation. A spectroscopic examination of these powders at the Naval Research Laboratory showed that luminescence was centered near 485 nm. From that date a thorough program was organized at Airtron to investigate the single crystal growth of $La Al_{1-x} Sc_x O_3$ compounds. This report summarizes the efforts made through the December, 1983 period under a portion of our growth program.

2.0 Experimental Procedures

2.1 Materials for Compositions

The starting components for all of our single crystal

preparations are lanthanum oxide (La_2O_3), aluminum oxide (Al_2O_3), scandium oxide (Sc_2O_3), and cerium oxide ($Ce\ O_2$). The components were purchased from recognized vendors in a purity which is considered to be laser or luminescent grade. Table I gives a general summary of the pertinent data. Overall it is thought that $Sc_2\ O_3$, because of its limited industrial use, cost, and relative scarcity, has the greatest amount of impurity. The impurity range of most 99.99% rare earth oxides is about 100 ppm of other rare earth ions and 100-200 ppm of non-rare earths. The latter are principally Ca^{2+}, Mg^{2+}, Si^{4+}, Fe^{3+}, Na^{1+} and Al^{3+}. It is important to note that with the purity of our materials, there is probably no effect whatsoever on the phase behavior. Under any circumstances these impurity levels are not detected by X-ray diffraction procedures.

A further word must be said about the $Ce\ O_2$ since the starting material is Ce^{4+} and the desired dopant is Ce^{3+} in the perovskite. In most oxide systems such as garnets, perovskites, or related structures the proportion of Ce^{3+} is thought to be high upon doping with $Ce\ O_2$ and growing in less than 1% of O_2. It can be made higher by growing under a reducing gas like H_2 or annealing the crystal in H_2 after growth. The amount of Ce^{3+} can be maximized by doping with $Ce_2\ O_3$ and growing in an inert or reducing gas. However the preparation of $Ce_2\ O_3$ is a fairly complicated procedure. It is prepared by H_2 or carbon reduction

TABLE I
MATERIALS USED IN PROGRAM

Component	Purities	Vendors
La_2O_3	99.999%	United Mineral & Chemical
Al_2O_3	99.999%	Baikowski International
Sc_2O_3	99.99 %	United Mineral & Chemical
$Ce\ O_2$	99.999%	Spex Industries

of Ce O_2 at 1200° C or higher. Once prepared it is fairly
stable unless oxidized directly at high temperatures. In all
of our experiments we have begun and retained the dopant with
Ce O_2. Since the amount of dopant is 100 - 500 ppm, one can
see that the Ce O_2 should have no effect on phase behavior to
a good approximation. However, the chemical state may influence
the presence, intensity, or other factors associated strictly
with the luminescent behavior.

2.2 Crucibles Used

The most useful crucibles for all of our preliminary
work were constructed from 99.95% iridium metal. Crucibles
were fabricated by Engelhard Industries. It should be realized
that the melting points of our component oxides range from
2050° C to 2400° C. The perovskite compositions of interest
probably melt at 2050°- 2200° C. Fortunately our early experi-
ments showed that stable melts could be obtained for prolonged
times without any damage to the crucible. In order to
obtain a complete melt in a crucible, the wall temperature is
about 50°- 150° hotter than the melt center. Iridium melts at
2450° C. The iridium crucible size was 2.00 inch diameter x
2.00 inches high with a volume of 103 cm^3. Wall thickness is
0.060 inch. All crucibles were used with lids which had a 1.25
inch circular hole for the crystal. There has been some
discussion[7] that the presence of Ir^{4+} and Fe^{3+} may cause
fluorescent quenching. This item is debatable but the growth

of crystals in molybdenum crucibles may be preferable for
reducing atmospheres.

Crucibles prepared from molybdenum, tungsten, or
tantalum are much more susceptible to oxidation than iridium.
However the pure metals have melting points of 2610°C, 3410°C,
and 2996°C, respectively. The metals are heated primarily
under vacuum, in reducing gases such as H_2, or in pure dry N_2.
We have attempted direct heating with 400 KHz RF in our standard
growth furnaces. An atmosphere of 99.75% N_2 -0.25% H_2 was passed
continuously through a sealed system. Our crucibles were made
from molybdenum and were 2.00 inch diameter x 2.00 inch high x
0.090 inch wall. Similar ones were made in a 3 x 3 inch size.
These were manufactured by Newark Spinning Co. from 99.95%
metal. The first attempts were made by heating the bare cruci-
ble to about 2000° C in order to check for evidence of severe
corrosion. Some oxide was formed but the crucible survived
intact. ˙By preparing a melt of La Al O_3 and running it at
temperatures close to 2100° C, we demonstrated the integrity
of the system. The general procedure on crucible choice was to
perform all preliminary growth and phase behavior experiments in
iridium. If and when luminescence quenching occurs, a switch
to molybdenum can be made using the same melts and growth
station geometry.

2.3 Seed Crystals

Our first compositions were prepared with the idea of

obtaining stable melts and attempted seeding on a bare iridium wire. The melts were brought to the position where a tiny island of solid material was evident on the melt surface. The temperature was increased until this last solid disappeared. The iridium wire was inserted and some crystallization always occurred. However the seeds were small and of an unknown and inconsistent orientation. Frequently a large polycrystalline mass was obtained. Better results were given by a piece of La Al O_3 obtained from Crystal Systems of Salem, Massachusetts. This was a translucent piece of twinned crystal melted in a Mo crucible. The best and most consistent results were obtained from a clear twinned single crystal of pure La Al O_3 grown by the Czochralski method. This crystal was about 4 - 5 mm diameter x 20 - 25 mm long and provided by Dr. Van Nicolai of ONR. The orientation was along [111] of the high temperature cubic phase. The crystal was used as received in the twinned state. This crystal always gave a seeded melt quickly and started growth with no complications. The seed was held in an iridium holder. The origin of this La Al O_3 single crystal was from work [8,9] performed by Union Carbide under contract to ONR.

2.4 Growth Station

The growth station used under this program was a typical RF heated Czochralski design similar to those used in the production of high melting oxide laser crystals. A picture of the actual station is given in Figure 1 while Figure 2 is a

Figure 1   Czochralski Growth Station
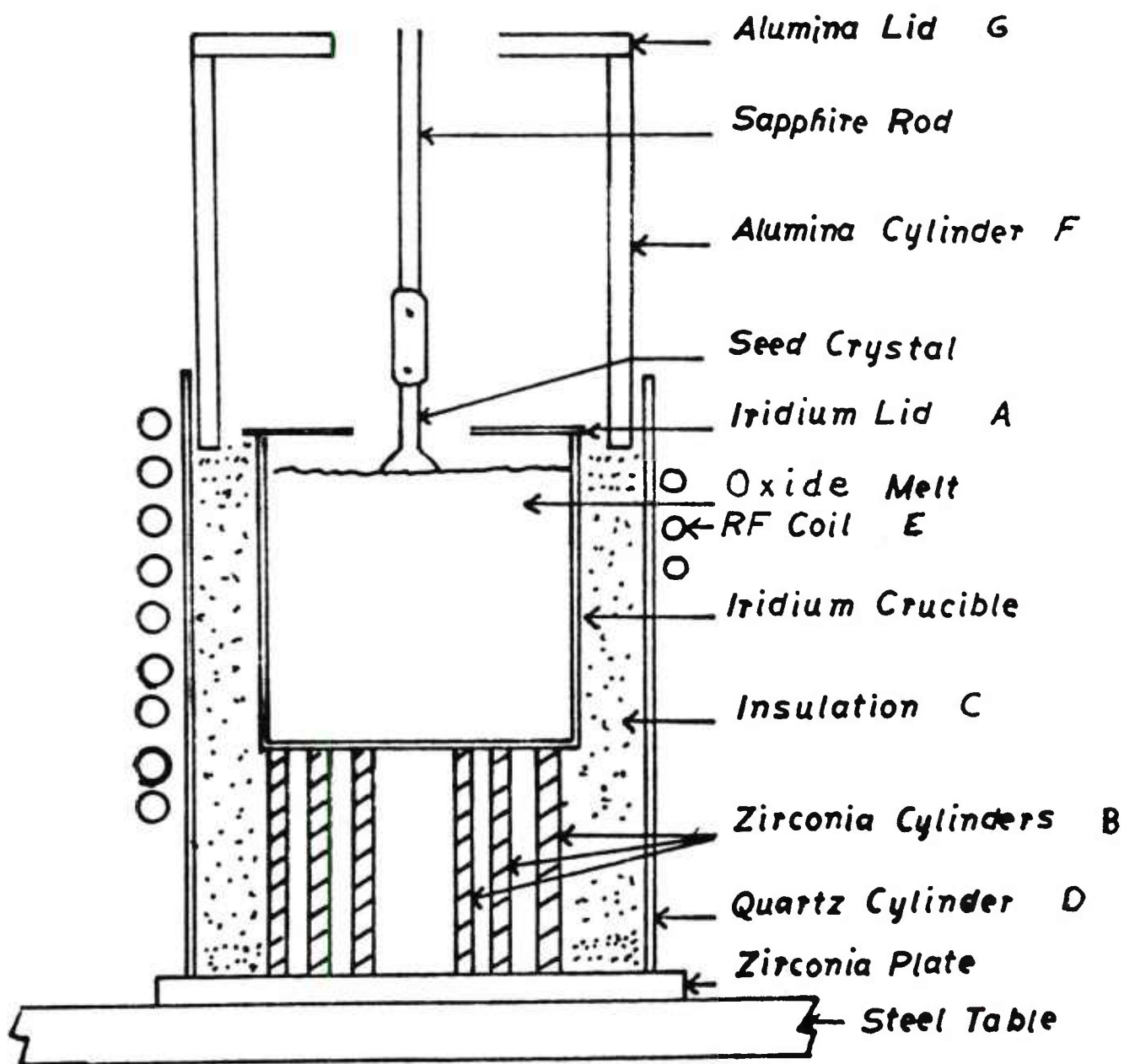
Figure 2   Drawing of Basic Growth Station

drawing of the crucible and insulating support materials. The RF unit is a Lepel Inc. 70 KVA, 400 KHz, commercial model culminating in a 10 turn copper coil. An optical pyrometer provided a signal used to control the diameter of the growing crystal. The crucible and appurtenances were surrounded with a sealed bell jar for atmosphere control. The growth gradient along the pulling direction was sufficient to get seeding initiated and crystals of 1-2 cm diameter x 5-10 cm could be grown without difficulty. Pulling and rotational mechanism arrangements are provided over a range of 0.1 - 10 cm/hr and 1-150 rpm respectively.

2.5 Run Technique

The general procedure for all runs remained the same. Preparations were chosen on the basis of the desired compositions. The pure oxides were weighed and mixed thoroughly. The oxides were packed in the crucible prior to each run. The melt volume and hence amount of the components was chosen to fill the crucible to about 80-90% of capacity at melt temperature. The crucible is placed in the station according to a precise and reproducible geometry. The bell jar is put over the system and gas flow is commenced. The crucible is brought to a temperature where all material is liquid. The seed crystal is then lowered into the melt and the latter is cooled to start growth. When growth starts satisfactorily, the control system is initiated and the crystal is brought out to the sought diameter. The crystal is

then pulled to total length. Usually the run is stopped with the grown crystal in contact with the melt to minimize thermal shock upon cooling. The station is programmed down from melting points of 2100-2200°C to 25°C over a period of several days. The crystal is removed by cutting or fracture at the bottom. The crucible is cleaned for the next run.

2.6 Crystal Compositions

Little or no previous work has been done on mixed perovskites involving the three component system [10] of La_2O_3 - Al_2O_3-Sc_2O_3. Only the two component systems are reported. The phase diagram is a serious omission and prevents one from going directly to a verified composition which will show some promise for growing a single crystal. In the absence of these data we have chosen to examine growth of single crystals in the formulation $La\,Al_{1-x}\,Sc_x\,O_3$ where x lies in the range of 0.15-0.30. The only rational justification for this is the coincident report [11] of a composition near x=0.30 made from sintered oxides at 1200°C (this composition was <u>not</u> a pure single phase as judged from the reported X-ray diffraction pattern). On the basis of size considerations it might also be argued that 25% substitution of Al by Sc might tend to give ordered cubic perovskites. However this is only suggested [4] and the highest degree of ordering is thought to occur when the two B ions are very different in size and charge. Galasso[4] does not report ordering

in our system but his book is complete to only 1970. Note that Al^{3+} and Sc^{3+} have the same charge and the ionic radii are 0.56A and 0.69A, respectively, as calculated by Geller[12] for ABO_3 type compounds. As far as a laser host is concerned, the crystal can be ordered or unordered, cubic or any other system, and of any composition. However, it <u>must</u> fulfill the emission and quality requirements desired for blue-green crystal lasers.

2.7 Atmospheres for Growth

The choice of gas for growing any single crystal material is highly important. Ideally, oxides should be grown in O_2, fluorides in F_2, and so forth in order to prevent defects such as vacant lattice sites. The latter usually lead to color center phenomena which may interfere with absorption or emission. One must also recognize the effects of the growth atmosphere on the desired valence states of any components. For example, the Ce^{3+} is a dopant which is best stabilized by no oxidizing conditions. For our purposes, the gas has no effect on any phase behavior. We have chosen a mildly reducing gas mixture of N_2-H_2 to introduce the Ce^{3+}. About 0.25-1.00% by volume of H_2 is satisfactory. So far as is known, this has not generated color centers. However, large single crystals have not been examined optically. It is known that the change of gas or elimination of H_2 will cause slight color shifts as observed visually. The use of large amounts of H_2 or the presence of H_2O may introduce small

concentrations of OH^- into oxide crystals at high temperatures.
The OH^- may act as a quenching center and affect fluorescent
yields.

2.8 Doping Levels of Ce^{3+}

The ionic radius of Ce^{3+} is very close to that of La^{3+}
and we have always assumed a distribution coefficient of 1.0 for
Ce^{3+} introduction into our melts. The absolute concentration of
Ce^{3-} in the melt was formulated to be 0.01 - 0.05 atomic %. This
is a rather low concentration compared to most laser crystals which
are doped at levels of 10-100 times higher than this. However,
the absorption and emission bands of Ce^{3+} are very strong and
0.05% is sufficient. We have made no attempts to measure
fluorescent lifetimes, or lifetime as a function of concentration.
The dopant of Ce^{3+} at 0.05% is never detected in X-ray diffrac-
tion patterns. Because of its similarity in size and chemical
activity to La^{3+}, we believe there is no effect on phase behavior
in all our work. Therefore, all crystal preparations contained
Ce.

2.9 Evaluation of Crystals

After a crystal was grown from a particular composition,
the boule was separated from the seed and examined visually and
microscopically. The color, crystallinity (single or polycry-
stalline), transparency, quality, and stability in light are
noted. The crystal is examined under a short wavelength ultra-

violet lamp for color and brightness of fluorescence. The
crystal is also sectioned into 1 mm disks. These disks are
mechanically polished on both sides and examined in a polari-
zing microscope for structure, twinning, phase separation, and
other artifacts. Finally, the crystal is sampled at the top
and bottom for X-ray diffraction analysis. The latter provides
direct evidence of structure, quality, phases, impurities, and
incorporation of Sc by means of lattice constant. In some
cases, the absorption and emission spectra were taken from poly-
crystalline powders. X-ray patterns were run over the full
range of 2θ values from 10 - 120° with Cu K_α radiation. Lat-
tice constants were measured from resolved doublets at high 2θ.
Both diffractometer and films were used to record patterns.
The films were given exposures of 24 hours to detect any weak
lines not apparent on a diffractometer trace. This is important
especially for detection of small amounts of a new phase or
evidence of ordering in perovskite compositions.

3.0 Results of Growth Runs

3.1 Run Description

Two problems which had to be overcome initially in this program were (a) to obtain material from which seeds could be fabricated for use in later runs, and (b) to obtain doped crystalline material which exhibited the desired fluorescence. Since the presence of atomic iridium in the crystal was believed to quench the Ce^{+3} fluorescence, it was felt that in order to solve the latter problem, iridium crucibles should be avoided if possible. Additionally, it was felt to be advantageous to avoid iridium because of the high melting point of $La\ AlO_3$ which requires the crucible to be driven near to its melting point. Consequently, the first growth experiment was made using a molybdenum crucible in an inert atmosphere of nitrogen containing approximately one percent hydrogen to control the valence state of cerium.

In spite of efforts to eliminate oxygen by purging and outgasing the system, it was not possible to grow using this arrangement. Extensive oxidation of the molybdenum occurred with the crucible glowing only red hot. Thus a completely closed system and inert environment are indicated.

The second growth experiment was designed to obtain single crystalline material from which to fabricate some seeds. The lack of success with molybdenum required that an iridium

crucible be used, but an approximately 0.25 percent hydrogen atmosphere was utilized to provide reducing conditions. An effort was made to obtain nucleation and growth on an iridium wire dipped into and pulled out of the melt, but, when this was unsuccessful, the entire melt was cooled with the wire in contact. This nucleation site allowed some single crystalline areas to develop as the melt cooled and slugs were core-drilled from these areas to obtain crystalline pieces for seeding. The cooled melt is exhibited in Figure 3. at the crucible bottom.

Following this experiment a makeshift iridium holder was fashioned and one of the pieces obtained in the previous growth run was used in an effort to obtain growth. This was only partially successful in that thermal asymmetry in the melt caused the growth to rotate eccentrically and prevent adequate control. Subsequently the melt was cooled with the seeded portion in contact and an improvement in the crystalline quality of the solidified melt was achieved. Crystalline pieces cut from the solidified melt as well as the iridium holder are exhibited in Figure 4.

In spite of these successes, it was felt that the low thermal gradient, the awkward shape of the seed holder and the size of the seeds obtained would preclude adequate control and quality of growth. At this point, a small La Al O_3 crystal became available and this crystal was shaped to provide a good

Figure 3.   Crystallized melt obtained by seeding with
           an iridium wire.

Figure 4. Initial La Alo₃ seeds with iridium holder.

quality seed of sufficient length. The fourth growth experiment
utilized this seed to obtain the crystal exhibited in Figure 5.
It should be noted that in this and the preceding experiments
the melt composition was adjusted to provide a 10% substitution
of scandium in the crystal. There was no immediate indication
of any effect this might have had but the quality of growth
was fairly good. Some cloudiness was evident but there was no
indication of a tendency toward cracking.

The fifth growth experiment was designed to provide a
25% substitution of scandium in the crystal. In order to accom-
plish this, the melt from the previous growth run was compo-
sitionally adjusted by adding additional powder to the crucible.
Unfortunately, the amount required to do this exceeded the
capacity of the crucible and it became necessary to terminate
the experiment and to clean the crucible.

The sixth growth run was again formulated to the 25%
scandium substitution. The melt had very good convection char-
acteristics and no difficulty was encountered in dipping the
seed or initiating growth. However, at some point after the
growth was put into its automatic mode, the crucible developed
a leak and the growth was terminated.

The seventh growth run was intended to repeat the
preceding experiment, but the crucible again developed a leak
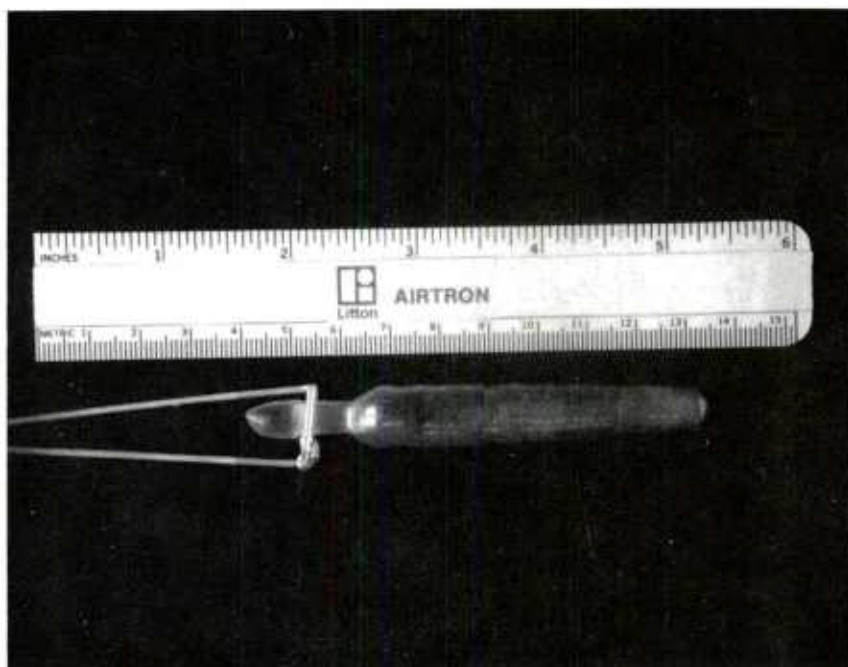and it was necessary to terminate the run. Consequently, this

Figure 5. Single crystal of La Al$_{0.9}$ Sc$_{0.1}$ O$_3$

experiment was carried over to the eighth growth run. Although the melt convection pattern looked good and the initial growth proceeded well, some problems were experienced in controlling the diameter in the automatic mode. It became necessary to control the growth manually in order to obtain sufficient growth on which to perform some x-ray measurements. Following termination of the growth cycle, the crystal assumed an opaque appearance characteristic of particulate inclusions (Figure 6). It appeared to be single crystalline although twinned.

At this point in the program, it was determined that the composition of the previous melts was determined incorrectly so that growth was carried out from what would appear to be incongruently melting alumina rich compositions. The x-ray data indicated that single crystalline $LaAlO_3$ was obtained but that the amount of scandium substitution was relatively small. An adjustment was made to achieve the 25% substitution in the ninth growth run, but after several growth attempts, the crucible leaked again.

The tenth growth experiment achieved the objective of obtaining a crystal having the desired 25% substitution. The growth quality was not good but it was improved over that achieved in the eighth growth run. The x-ray data also confirmed that the scandium was now entering the crystal lattice as anticipated. This crystal can be observed in Figure 7.

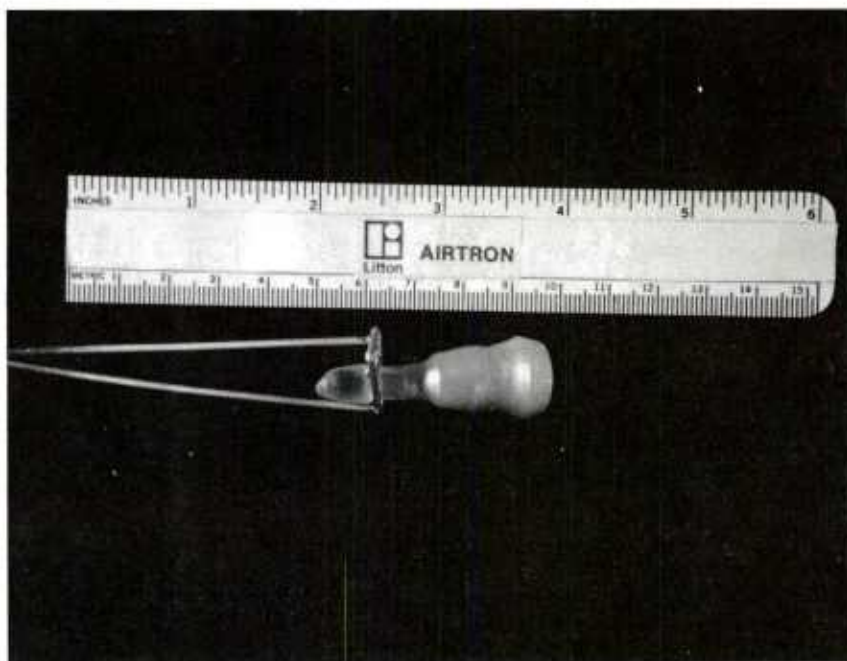The eleventh growth run carried the experiments one

Figure 6. Single crystal of La Al$_{0.75}$ Sc$_{0.25}$ O$_3$ grown off stoichiometry
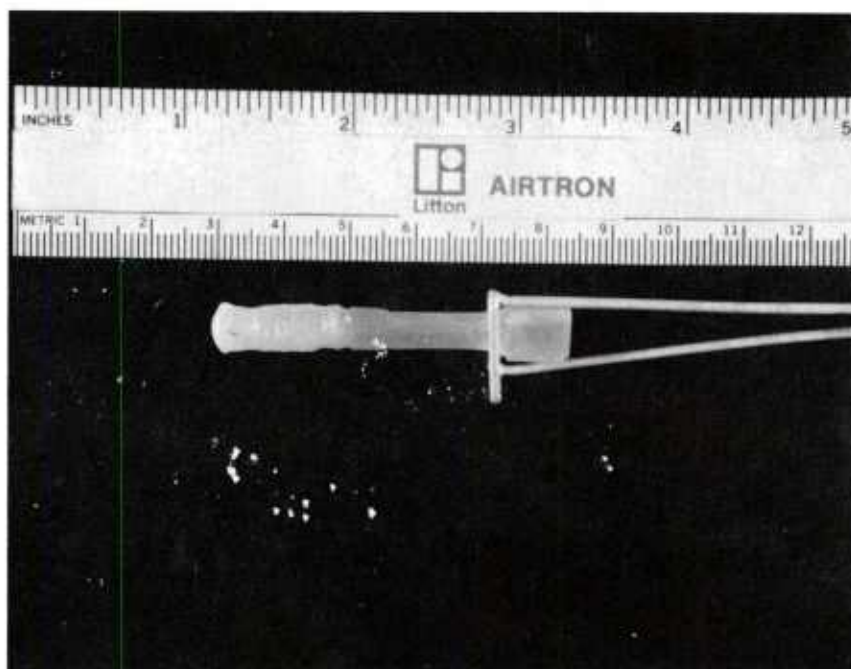
Figure 7. Single crystal of LaAl$_{0.75}$Sc$_{0.25}$O$_3$ grown with a correct melt formulation.

step further in that it was designed to accomplish a 30% substitution of scandium. As in previous runs, it appeared to be a single crystal but was opaque. However, x-ray measurements showed that a further substitution of scandium had occurred.

The growth experiments did not result in any high quality growth, but they did provide enough information to indicate a probable compositional region in which to work. It is felt that better results would have been achieved with better quality seeds and that further work at some fixed composition should result in that end. This would at least provide better material with which to carry out further growth experiments. Results of the growth experiments and growth conditions are summarized in Table II. It should be noticed that the crystal compositions were those originally formulated for the melt. They are not the actual analyzed composition of the grown crystal. It appeared that a distribution coefficient of 0.7 for Sc(crystal)/Sc(melt) is operative. All crucibles were iridium except for the first attempt. Some runs were attempted at both the 1.5 mm/hr pull rate and a slower one of 0.5 mm/hr to improve quality. However this made little difference in the cloudy appearance of the crystal.

TABLE II

SUMMARY OF CRYSTAL GROWTH RUNS

RUN #	CRYSTAL COMPOSITION DESIRED	CRUCIBLE MAT'L	PULL RATE (mm/hr)	ATMOSPHERE	COMMENTS
LA-1	$LaAl_{0.9}Sc_{0.1}O_3$	Molybdenum	--	1.1% H_2	Unable to Melt material due to excessive crucible oxidation
LA-2	$LaAl_{0.9}Sc_{0.1}O_3$	Iridium	--	0.25% H_2	Melt solidified for seed material
LA-3	$LaAl_{0.9}Sc_{0.1}O_3$	Iridium	--	0.1% H_2	Melt crystalized with single crystal piece in contact
LA-4	$LaAl_{0.9}Sc_{0.1}O_3$	Iridium	1.5	0.1% H_2	Translucent crystal of fair quality obtained
LA-5	$LaAl_{.75}Sc_{0.25}O_3$	Iridium	--	0.1% H_2	Run terminated due to inability to adjust melt composition
LA-6	$LaAl_{0.75}Sc_{0.25}O_3$	Iridium	--	0.1% H_2	Run terminated by crucible failure
LA-7	$LaAl_{0.75}Sc_{0.25}O_3$	Iridium	--	0.1% H_2	Run terminated by crucible failure
LA-8	$LaAl_{0.75}Sc_{0.25}O_3$	Iridium	1.5	0.1% H_2	Opaque single crytstal obtained
LA-9	$LaAl_{0.75}Sc_{0.25}O_3$	Iridium	--	0.1% H_2	Run terminated by crucible failure
LA-10	$LaAl_{0.75}Sc_{0.25}O_3$	Iridium	--	0.1% H_2	Translucent crystal of poor quality obtained
LA-11	$LaAl_{0.75}Sc_{0.25}O_3$	Iridium	--	0.1% H_2	Opaque single crystal obtained

3.2 X-Ray Data

In the absence of firm phase diagram studies, most of our information had to be obtained empirically from the crystal growth runs. The use of X-ray diffraction patterns is indispensable in judging what phases, crystal structures, or other phenomena may be present. Thus each grown crystal was sampled at the top of the boule and an X-ray diffractometer trace was run well into the high 2θ region. Since it was important to determine the presence of impurities in low concentration, many X-ray patterns were obtained also by film procedures. The latter were taken with exposures up to five times normal in order to verify the presence of very weak lines unambiguously.

Figure 8 shows the compositions we have investigated in the three component system of La_2O_3-Al_2O_3-Sc_2O_3. Most of these are located near the $LaAlO_3$ compound since increasing amounts of Sc_2O_3 were added normally to the melt in each run. The first few runs did indeed show that in the crystal, increasing amounts of Sc_2O_3 were incorporated. This was verified by the expanded lattice constant of the compositions. It should be recalled that the normal room temperature crystal form of $LaAlO_3$ is rhombohedral. If we assume that this structure is retained approximately with little difference in angle, then a "lattice constant" - composition curve may be constructed as in Figure 9. The largest value of the lattice constant we have observed is about 3.85 A which corresponds to an x of 0.25-0.30 in the formulation $LaAl_{1-x}Sc_xO_3$.
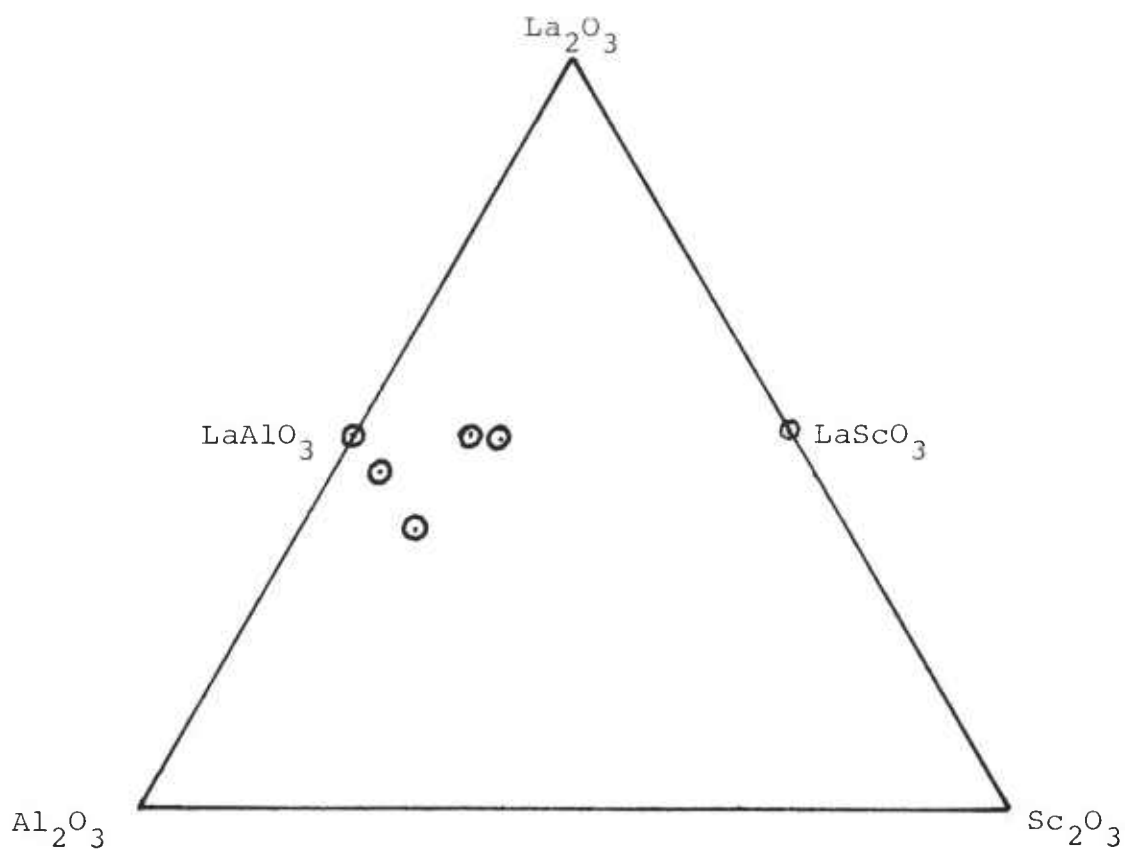
Figure 8 Compositions Investigated
in the La_2O_3 - Al_2O_3 - Sc_2O_3 System
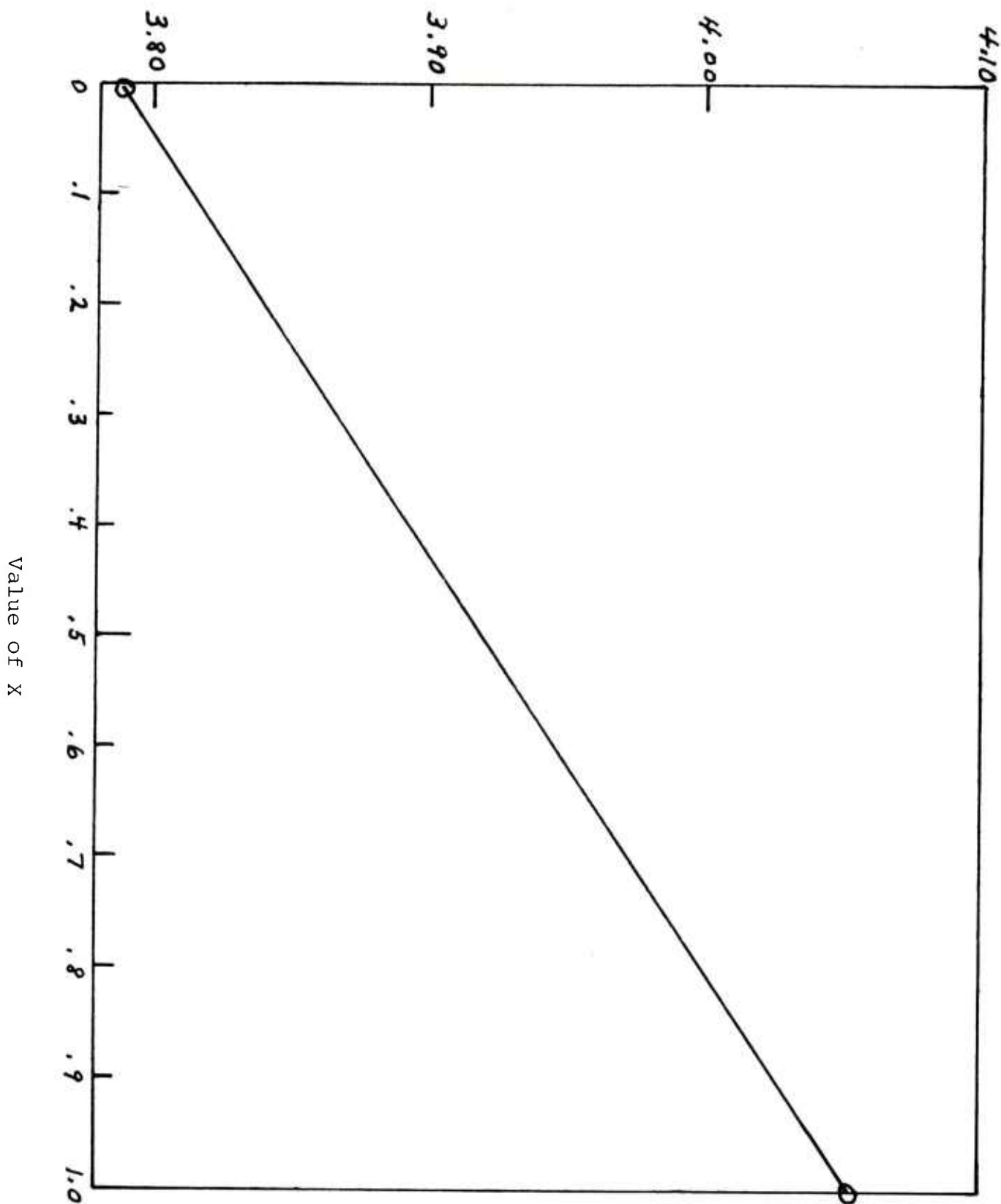
Figure 9 - Lattice Constants of La Al$_{1-x}$Sc$_x$O$_3$ Mixed Crystals

The actual values of x in the melt are larger than in the crystal which suggests that an effective distribution coefficient of 0.6-0.7 is necessary for k_{Sc}. At the highest values of x in the melt, it appears that a two phase liquid is obtained and any single crystal growth becomes difficult.

We reproduce in Table III some pertinent X-ray powder data. The values in columns 1 and 2 are experimental ones taken from a pure phase of $LaAlO_3$. In fact these were taken from our seed crystal and they agree perfectly with the reported data of Geller and Bala.[5] The values of columns 3 and 4 are calculated from the cubic pseudo cell which corresponds to a cubic perovskite material. Note that the true symmetry is rhombohedral and only at elevated temperatures is there a transition to the cubic phase. The data in columns 5 and 6 are calculated from an expanded cubic unit cell of larger dimensions. These of course do not fit the room temperature data but are listed for reference. Table IV is a film powder pattern taken at a long exposure to develop any weak lines. Notice that several of these are obtained at low 2θ angles. It is interesting to note that this pattern is from a cloudy but good single crystal. None of the weak or extra lines in the pattern correspond to the strong X-ray lines of the starting components or other combinations. Thus the pattern is due to the crystal but with some modification of the structure beyond the normal rhombohedral. The most troublesome features are the four very weak lines beyond the 3.85 A strong line. The latter is almost

Table III

X-ray Data for Pure LaAlO$_3$

Rhomb. hkl	d obs.	d calc. from $a_o=3.797$	Closest Cubic hkl	d calc from $a_o=7.583$	Cubic hkl
110	3.797	3.797	100	4.378	111
				3.792	200
10$\bar{1}$, 211	2.657	2.685	110	2.680	220
				2.286	311
1$\bar{1}\bar{1}$, 210	2.286				
200	2.188	2.192	111	2.189	222
222	1.896	1.899	200	1.896	400
220	1.736			1.740	331
20$\bar{1}$, 311	1.696	1.698	210	1.696	420
21$\bar{1}$, 321	1.548	1.550	211	1.548	422
				1.459	511
				1.459	333
21$\bar{1}$, 310, 332	1.342, 1.339	1.342	220	1.340	440
20$\bar{2}$, 422	1.264	1.266	300	1.264	600
				1.214	531
30$\bar{1}$, 330, 411, 433	1.199	1.201	310	1.199	620
32$\bar{1}$					

Table IV
X-ray Powder Data for Sample La-11

Observed d (Å)	Intensity	Calculated d a = 5.444 Å = 60.1°	hkl
8.733	vvw		
7.158	vvw		
6.242	vvw		
5.038	vvw		
3.853	vs	3.853	110
3.022	vvw		
2.719	vvs	2.722	211
2.321	vvw	2.323	210
2.233	vs	2.225	200
2.213	w		
1.929	vs	1.926	220
1.725	ms	1.767 / 1.722	311 / 321
1.579	vs	1.573	310
1.568	mw		
1.368	m	1.363	$20\bar{2}$
1.361	m	1.361	422
1.289	mw	1.284	411
1.221	s	1.219	$32\bar{1}$
1.165	mw		
1.117	w		
1.111	vw		

always the strongest and largest d spacing in any of the perovskite like structures. In addition to these four weak lines, there are several other weak additional lines at various spacings. These weak lines do not correspond to any of the components. Furthermore the strong line at 1.724 A does not show good agreement with calculated data. Part of this may be due to the angle chosen for α. However a more radical change in structure is suggested.

3.3 Visual and Microscopic

It was mentioned above that all of the grown crystals were of one detectable phase by X-ray diffraction. Visually, the crystals were not clear enough to get light through. In fact, they were never as clear as the original seed of La Al O_3 even though the latter contained a large number of micro twins. A good example of the type of crystal we obtained is given in Figure 10. Other examples are evident in some of the previous photographs of growth runs.

·In order to examine the single crystals, they were sectioned in a 1mm slice cut normal to the growth axis. The pieces were polished to a window specification with common abrasives in our polishing facility. Under a microscope, small scattering sites could be seen. These were similar to effects observed previously in Y Al O_3 and must be attributed to small amounts of an alternate phase. Crystal compositions which were prepared at another contractor showed the same behavior below the melting point,[13] It is also obvious from both the X-ray and microscope data that none of the prepared compositions were cubic at room temperature.
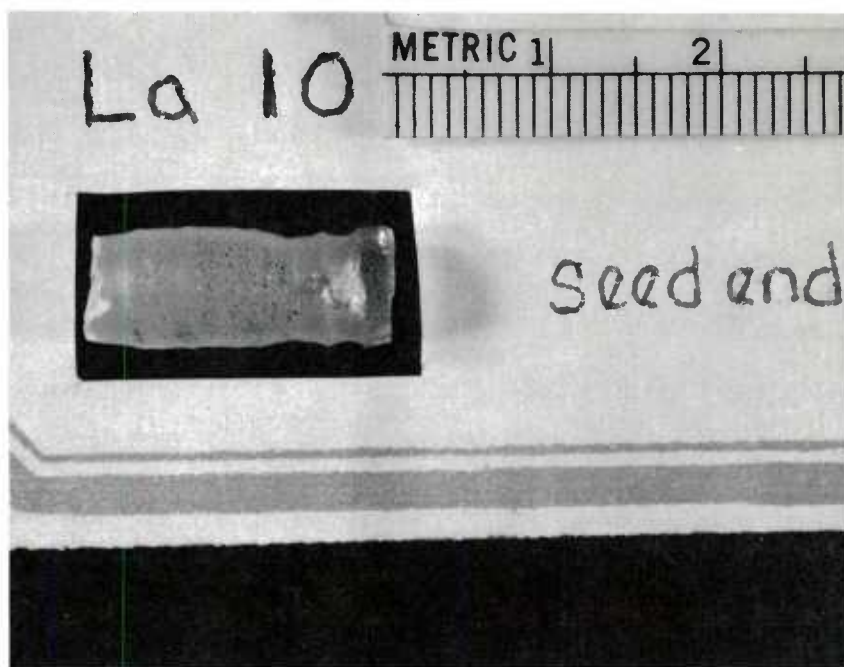
Figure 10. Example of grown crystal from Run
La-10

3.4 Discussion

It is difficult to assign all the reasons for not obtaining a cubic phase in the La $Al_{1-x}Sc_xO_3$ system. One of the fundamental criteria for a stable cubic structure is the Goldschmidt [14] tolerance factor t= $R_A+R_B/\sqrt{2}\overline{(R_A+R_B)}$ where R_A is the radius of the 12 coordinated cation (La) and R_B is the radius of the 6 coordinated cation (Al or Sc). For a stable range, t must be 0.8 $\leq$ t $\leq$ 0.9. If the La = 1.14, Al = 0.56, and Sc = 0.69 - 0.75, then t = 0.92 for La Al O_3, t $\geq$ 0.96 for La Sc O_3. Thus, for the mixed crystal of La Al Sc O_3, it would appear that t value is borderline or exceeds the desired value. It should be remembered that the ionic radii are preferably derived from X-ray data taken on actual perovskite materials. The paucity of data for Sc leaves some doubt as to what its radius actually is when combined with different elements. Even the mineral perovskite (Ca Ti O_3) does not have a cubic structure. The analog Sr Ti O_3 does and it has a t of 0.86. Since most tolerance rules are based on hard sphere packing, they are only approximate; the nature and type of bonding is also important.

It also appears that ordering phenomena appear more readily in compounds where the charge of the various B ions is different; for example the Al^{3+} and Sc^{3+} are similar whereas a Mg^{2+} + Ge^{4+} pair may order easily. Again, the charge type may influence the crystal structure more than a simple space consideration. Complex perovskites such as Ba $(Y_{0.5}Ta_{0.5})$ O_3 and Ba $(Mg_{0.33}Ta_{0.67})$ O_3 show a considerable degree of ordering. It should be noted that ordering can

3.4 Discussion - (Continued)

occur not only in cubic structures but other ones just as well.
For purposes of obtaining correct fluorescence emission, it
is preferred to have a precise crystal field with no
complicating distortions.

3.5 Recommendations

Literally hundreds of compounds are possible with the
perovskite (ABO_3) crystal structure or a distorted variation of
it. Thus, we can recommend that a careful approach must be
made with those compounds, which to a first approximation, may
give a cubic crystal structure from ion size considerations.
Combinations of La, Gd, Y, Sc, Lu for A ions must be sought to
give a high band gap host. The remaining ions of Al, Ga, Sc,
or In are used as B ions to adjust melting range. Ideally, the
materials for most perovskites can be prepared first in poly-
crystalline form. The presence of a cubic or other phase can
be checked by X-ray diffraction. If results are positive, then
the phase diagram should be investigated further. Finally, the
single crystal growth should be attempted when enough knowledge
is available on phase behavior. It should be realized that the
Ce^{3+} emission in these preparations must center near 485mm.
Fortunately, the fluorescence spectra can be obtained early
enough on the polycrystals.

4.0 Preparation of Fluorides

4.1 Background of $KMgY_3F_{12}$

Several rare earth and transition metal doped material preparations for the single crystal modified Czochralski growth of KMg_3F_{12} were scrutinized for their possible laser characteristics. The host crystal $KMgY_3F_{12}$ was assumed to be an isotype of the reported compound $KMnEr_3F_{12}$ [15] which has a tetragonal unit cell with a = 8.118A and c = 11.517A. The phase diagram of the $KMnF_3$ -ErF_3 system shows the existence of $KMnEr_3F_{12}$ at 75 atomic% ErF_3 at about 985°C. The extent of substitutions which are isotypical were discussed briefly by G. Labeau and M.F. Gorius in France. [15] Our work is an extension of one of these isotypes where we have attempted five different dopants as listed: 0.25 atomic % Ce, 0.25 atomic % Pr, 0.5 atomic % Cr, 1.0 atomic % Nd, and one codoping of 0.5 atomic % Cr with 1.0 atomic % Nd.

In the cases of Ce, Pr, and Nd we assumed that the dopant substituted for the yttrium sites in the crystal lattice. For the transition metal Cr^{3+} however, we assumed that the dopant substituted for the magnesium sites. The working formula $KMg_{1-y}Cr_yY_{3-x}Nd_xF_{12}$ was applied in the codopant substitution case.

4.2 Fluoride Preparation and Growth

The fluoride materials prepared were all subjected to the following hydrofluorination process:

A) Oxide materials of at least 99.99% purity reacted in anhydrous

hydrofluoric acid at 1000°C.

B) Fluorinated oxide material was sintered at 1000°C and then elevated to a temperature of approximately 1175°C for four hours to attempt further sintering and melting.

C) Fluoride material was cooled in the reactor for 3 hours to room temperature. The reactor was purged with N_2 to remove residual HF gas.

A picture of the hydrofluorination reactor furnace is provided in Figure 11. A platinum tube resistance furnace with water cooled end ports is the primary furnace. Gas ports through end caps provide gas flow through the reactor to a potassium hydroxide scrubber system whereby the byproducts of KF and H_2O are collected. Most starting materials were 5-9's purity except for the Ti dopant metal at 4-9's. All materials prepared were stored in a sealed container and placed in a desiccator. The following is a list of materials prepared.

1) $Ce_{0.00225} K Mg Y_{2.9975} F_{12}$

2) $Pr_{0.0025} K Mg Y_{2.9975} F_{12}$

3) $Cr_{0.005} K Mg_{0.995} Y_3 F_{12}$

4) $Nd_{0.01} K Mg Y_{2.99} F_{12}$

5) $Cr_{0.005} Nd_{0.03} K Mg_{0.995} Y_{2.97} F_{12}$

6) $Ti_{0.0011} Li Y_{0.999} F_4$
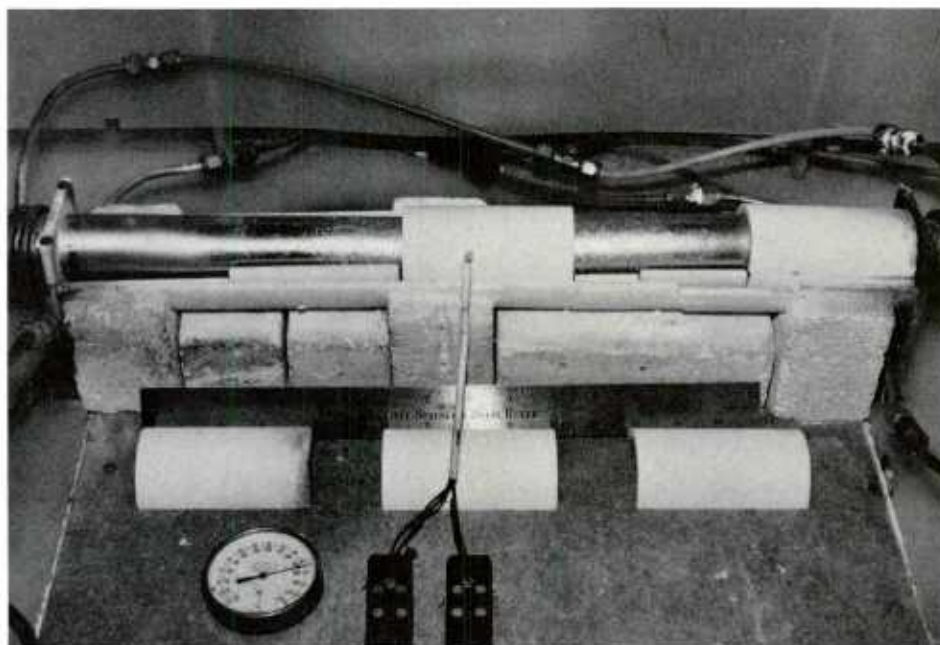
7) $Ba Y_{1.96} Er_{0.04} F_8$

Figure 11.   Platinum hydrofluorination apparatus

Not all prepared materials were used for single crystal growth by modified Czochralski techinques. Only the Pr, Ti and Ba materials received attention first. The picture of Figure 12 shows the station used for the growth of single crystals. Crystal diameter was controlled by use of a weight signal processed through a temperature feedback loop. A reactive atmosphere above the melt was maintained throughout the entire growth cycle. The station incorporated 2% HF in N_2 as the carrier gas.

The furnace itself had platinum wound resistance heating elements which surround the long central platinum tube liner where a HF reactive atmosphere is maintained. The HF gas is collected and neutralized through the scrubbing system. During the Ti run, $2\%H_2$ was also added to the gas stream so as to maintain Ti^{3+} valence state. Before all growth runs the station is first subjected to an evacuation procedure which removes most oxide contaminants. Five or six evacuation N_2 purges are performed before heating and melting any material in the HF reactive atmosphere. Normal pull rates for new experimental runs was 0.030 in/hr.

4.3 Growth Results

Each of the seven new materials will be discussed individually:

1) $Ce_{.003}$ K $Mg_{2.997}$ F_{12} - a polyrystalline preparation sintered in situ. Material samples were sent out for evaluation. No single crystal growth was attempted.

Figure 12. Growth station for fluorides

2) $Pr_{.003} K Mg Y_{2.997} F_{12}$ - a polycrystalline preparation was
sintered in a crucible but not melted. Clear material resulted
from the hydroflorination process. Some material was sent out
for evaluation and the first trials for growth of single crystals
were performed in September of 1984. Eight attempts were made
thus far to attain cm size pieces of good material for orientated
growth. It appears that the prescribed 25 mole % $K Mg F_3$ and 75
mole % composition may need to be changed slightly in order to
facilitate seeding and inclusion free growth. It seems that thus
far the crystals want to grow readily, however, the quality thus
far lends characteristics which may indicate a compositional
problem. No X-ray work has been done to attain an oriented seed.
It is worth noting here that the material grown thus far has
been done in 1.5" x 1.5" crucible technology which is not pre-
ferred. Our more recent technological advances for proper fur-
nace profiling are geared toward 2" x 2" or 2.5" x 2.5" crucibles.
It would be more advantageous to work with slightly larger melts
for future research.

The following five pictures (Figure 13-17) were taken during
the latest experiments and show the progress made thus far in mod-
ified Czochralski growth of $Pr: K Mg Y_3 F_{12}$. These attempts were
all from a 1.5" x 1.5" crucible. Technological advances have
recently been made in furnace design so as to facilitate growth.
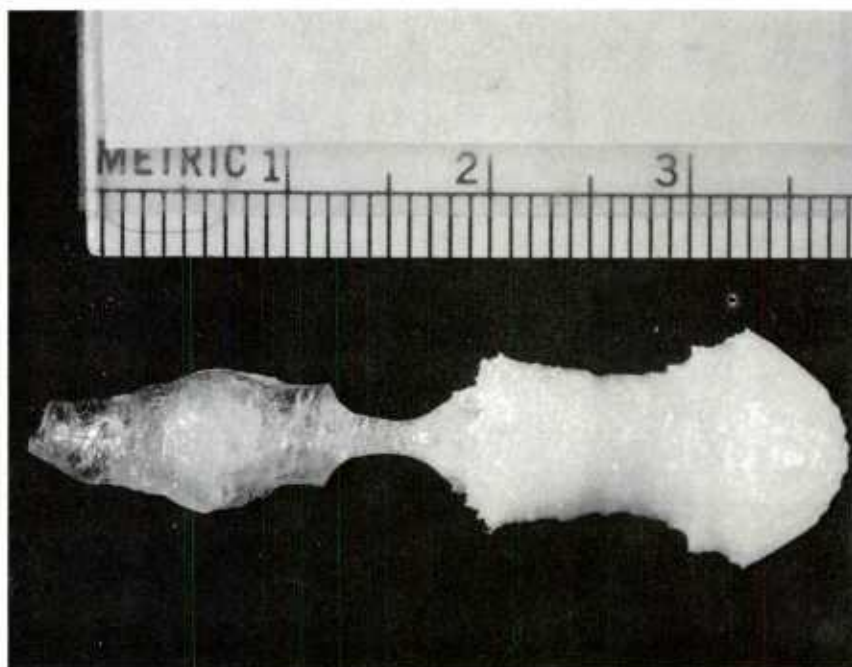
Figure 13.   First seed crystals of 0.25 atomic % Pr:KMgY$_3$F$_{12}$
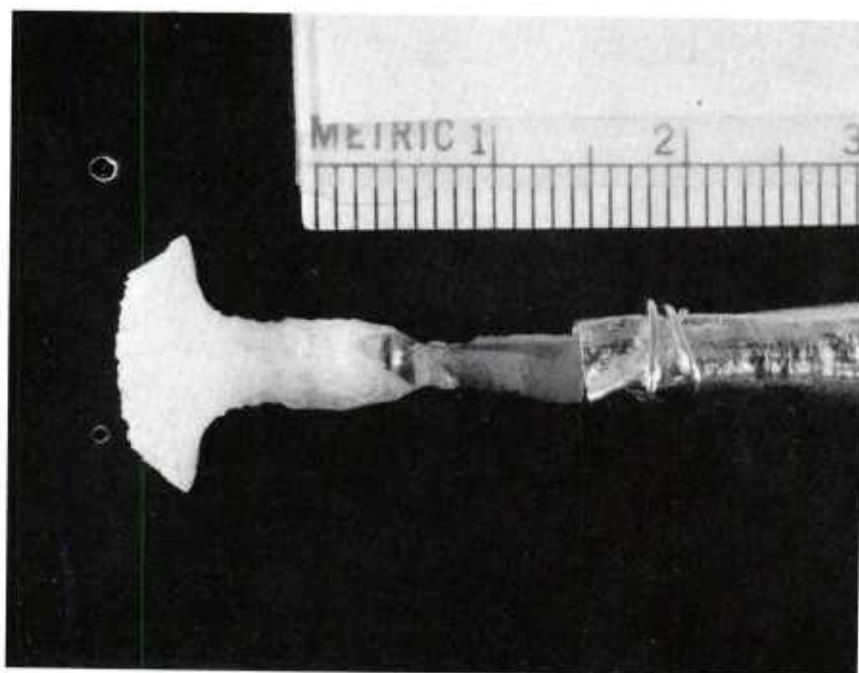grown by seeding with a platinum rod.

Figure 14. Second attempt to grow seed material
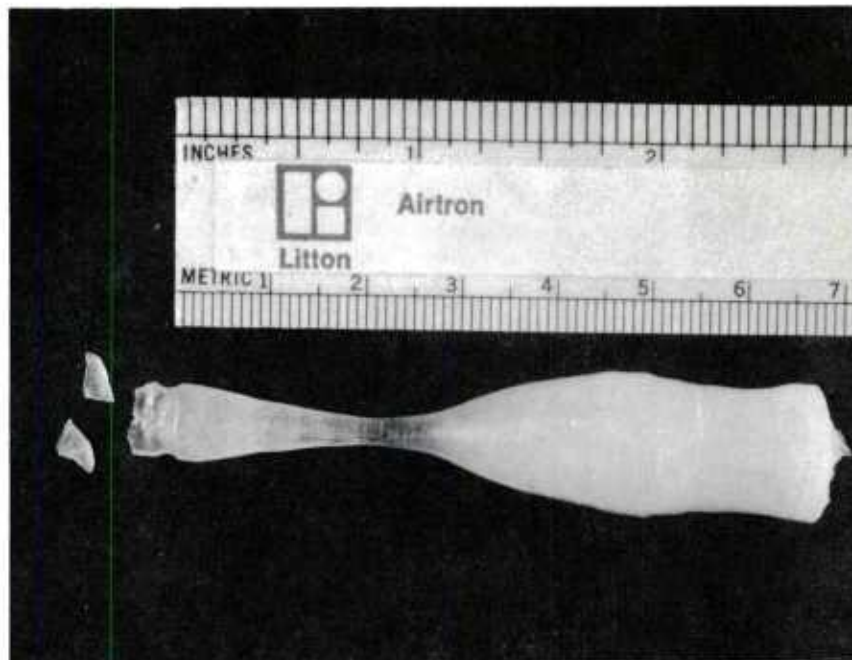
Figure 15. Third attempt to grow seed material

Figure 16.   First crystal grown from prior seed
material. (Growth axis was randomly
preferred.)
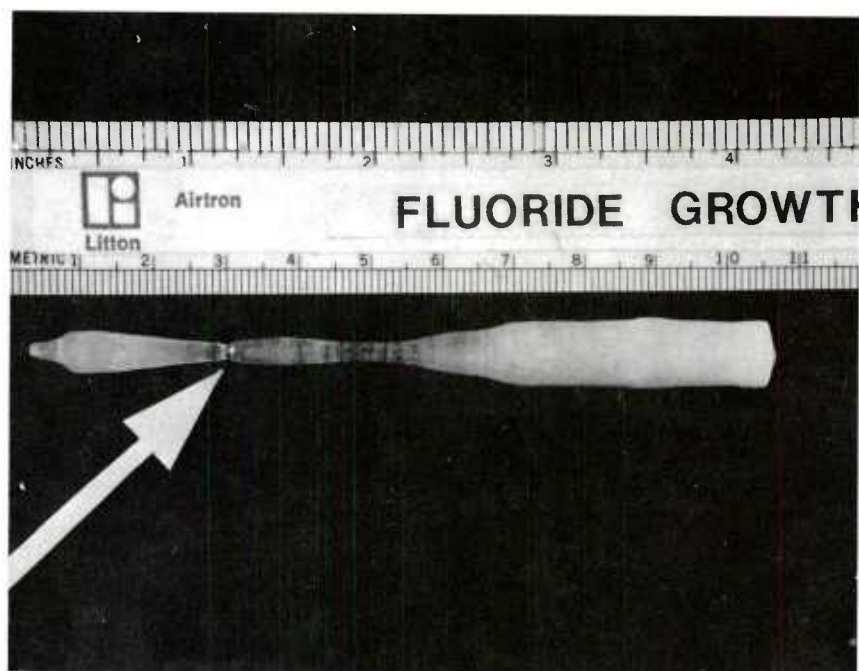
Figure 17.   Second crystal grown using the first
crystal as a seed.   Growth axis still
unidentified but preferred thus far.

One major factor is crucible size to enable growth of flat inter-
face materials. This should produce the best quality synthetic
material possible. Under these new growth conditions more con-
fidence can be placed in yield factors expected. This advance
can have direct impetus toward time and labor savings.

3) $Cr_{0.005}$ K $Mg_{0.995}Y_{M3}$ F_{12} - a polycrystalline preparation was
sintered in nature but not melted. Cr seems to be seggre-
gated in randomly located small areas throughout the melt.
However, looks like it is uniform throughout the bulk of the prep-
aration. No single crystal growth has been attempted. Material
samples were sent out for evaluation and characterization.

4) $Nd_{.01}$ K Mg $Y_{2.99}$ F_{12} - a polycrystalline preparation sin-
tered in nature, not melted, but fully reacted resulted. Uni-
form Nd distribution throughout the bulk. No growth was attemp-
ted. Material samples were sent out for evaluation and chara-
cterization.

5) $Cr_{.005}$ $Nd_{.003}$ K $Mg_{.995}$ $Y_{2.997}$ F_{12} - a polycrystalline pre-
paration sintered in nature, not melted, but fully reacted re-
sulted. Hard to describe Cr distribution through the bulk be-
cause some was locally concentrated and some was uniformly dis-
tributed. No growth was attempted. Material samples were sent
out for evaluation and characterization.

6)$Ti_{.001} Li_{.999} F_4$ - A single crystal was prepared by reacting Ti metal with HF in a platinum reactor using a graphite boat at a temperature of 840-870°C for four hours to yield $Ti F_3$, which was stoichiometrically mixed with YF_3 prepared similarly but at higher temperatures and LiF which was commercially purchased from Harshaw Chemical Company.

Ti:YLF was grown after a clear undoped YLF run was made in our ASTRO furnace. No changes were made in the growth environment except Ti:YLF was grown at 0.020"/hr. full rate rather than 0.050"/hr. for $LiYF_4$. The resulting boule appeared clear except for close examination where one can see random fine type scatter sites which were only seen with use of a HeNe laser with a 1 MM beam.

A cathodoluminescent emission spectra for a sample of undoped YLF was compared with that of the new Ti:YLF and a broad peak was found for Ti:YLF centered at 490 nm. No peaks were seen in the undoped YLF.

Future work needed in this system.

1) X-ray diffraction powder pattern for identification of structure and to check for impurity lines.

2) Absorption and transmission spectra.

3) Lasing parameters for possible applications.

A higher Ti doping concentration may be desirable too.

7) 2 atomic % Er in Ba $Y_{1.96}$ $Er_{.04}$ F_8 crystal.
A 350 gram preparation was made for #147-BYF run which yielded
a 140 gram single crystal ready for seeds, parts and evaluation.
The resulting crystal had a slightly concave interface this time.
Future runs will definitely yield better crystals.

5.0 Conclusions

The $La Al_{1-x} Sc_x O_3$ system has been investigated as a likely host crystal to give blue-green emission when doped with Ce^{3+}. Nearly 10-12 attempts were made to grow single crystals over a compositional range up to x=0.3. Seed crystals of pure $La Al O_3$ were used in $[111]$ orientation. In all crystals, trace amounts of an apparent second phase were the principal problems. Even at slow growth rates, cloudy crystals were obtained which greatly impaired the optical quality for laser purposes. The complete phase diagram was not determined for the three component system $La_2 O_3 -Al_2O_3 -Sc_2O_3$ but it appears that the growth problems are too severe for meaningful improvements. The full exploitation of the perovskite structure still offers hope for cubic mixed crystals which may fulfill conditions for a satisfactory laser host.

Several fluorides of mixed crystal type were investigated as part of our program for examining possible blue-green lasers and hosts. The first important system was $KMgY_3F_{12}$. This material, which can incorporate both first transition series elements and rare earths, was grown in small single crystals and appears to be congruently melting. Polycrystalline preparations were prepared with Ce^{3+}, Pr^{3+}, Nd^{3+}, Cr^{3+}, and Nd^{3+}. These samples were evaluated for spectroscopic purposes. Most of the single crystal work was performed with the Pr^{3+} dopant.

A sizable crystal of fair quality was obtained and should be useful for future experiments. Two other systems were examined under our program. A crystal of Er^{3+}:BaY_2F_8 was grown easily. This material is of some use for 2.94μm lasing at high doping levels of Er. The single crystal of $YLiF_4$ was also doped with Ti^{3+}. This system may have some use for a tunable laser.

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